AHBC4043

# MULTI-LAYER FUEL AND VAPOR TUBE-NYLON 6/EVOH/NYLON-6

## I. RELATED APPLICATIONS:

This application is a continuation-in-part of Serial Number 07/868,754, filed April 14, 1992 currently pending before the United States Patent and Trademark Office.

## II. Field of the Invention:

The present invention relates to a hose for use in a motor vehicle. More particularly, the present invention relates to a multi-layer hose which can be employed as a fuel line or vapor recovery line in a motor vehicle.

## III. Background of the Invention:

Single layer fuel lines and vapor return lines of synthetic materials such as polyamides have been proposed and employed in the past. Fuel lines employing such materials generally have lengths of at least several meters. It is important that the line, once installed, not materially change during the length of operation, either by shrinkage or elongation or as a result of the stresses to which the line may be subject during use.

It is also becoming increasingly important that the lines employed be essentially impervious to hydrocarbon emissions due to permeation through the tubing. It is anticipated that future Federal and state regulations will fix the limit for permissible hydrocarbon emissions due to permeation through such lines. Regulations which will be enacted in states such as California will fix the total passive hydrocarbon emission for a vehicle at 2 $g/m^2$ per 24 hour period as calculated by evaporative emission testing methods such as those outlined in Title 13 of the California Code of Regulations, section 1976, proposed amendment of September 26, 1991. To achieve the desired total vehicle emission levels, a hydrocarbon permeation level for the lines equal to or below 0.5 $g/m^2$ per 24 hour period would be required.

Finally, it is also imperative that the fuel line employed be impervious to interaction with corrosive materials present in the fuel such as oxidative agents and surfactants as well as additives such as ethanol and methanol.

Various types of tubing have been proposed to address these concerns. In general, the most successful of these have been co-extruded multi-layer tubing which employ a relatively thick outer layer composed of a material resistant to the exterior environment. The innermost layer is thinner and is composed of a material which is chosen for its ability to block diffusion of materials such as aliphatic hydrocarbons, alcohols and other materials present in fuel blends, to the outer layer. The materials of choice for the inner layer are polyamides such as Nylon 6, Nylon 6.6, Nylon 11, and Nylon 12.

Alcohol and aromatic compounds in the fluid conveyed through the tube diffuse at different rates through the tubing wall from the aliphatic components. The resulting change in the composition of the liquid in the tubing can change the solubility thresholds of the material so as, for example, to be able to crystalize monomers and oligomers of materials such as Nylon 11 and Nylon 12 into the liquid. The presence of copper ions, which can be picked up from the fuel pump, accelerates this crystallization. The crystallized precipitate can block filters and fuel injectors and collect to limit travel of the fuel-pump or carburetor float as well as build up on critical control surfaces of the fuel pump.

In U.S. Patent Number 5,076,329 to Brunnhofer, a five- layer fuel line is proposed which is composed of a thick corrosion-resistant outer layer formed of a material known to be durable and resistant to environmental degradation such as Nylon 11 or Nylon 12. The tubing disclosed in this reference also includes a thick intermediate layer composed of conventional Nylon

6. The outer and intermediate layers are bonded together by a thin intermediate bonding layer composed of a polyethylene or a polypropylene having active side chains of maleic acid anhydride. An thin inner layer of aftercondensed Nylon 6 with a low monomer content is employed as the innermost region of the tubing. The use of Nylon 6 as the material in the inner fluid contacting surface is designed to eliminate at least a portion of the monomer and oligomer dissolution which would occur with Nylon 11 or Nylon 12. The thin innermost layer is bonded to the thick intermediate layer by a solvent blocking layer formed of a copolymer of ethylene and vinyl alcohol with an ethylene content between about 30% and about 45% by weight. The use of a five layer system was mandated in order to obtain a tubing with the impact resistance of Nylon 12 with the low monomer/oligomer production of Nylon 6. It was felt that these characteristics could not be obtained in a tubing of less than five layers.

In U.S. Patent Number 5,038,833 also to Brunnhofer, a three-layer fuel line without the resistance to monomer/oligomer dissolution is proposed in which a tube is formed having a co-extruded outer wall of Nylon 11 or Nylon 12, an intermediate alcohol barrier wall formed from an ethylene-vinyl alcohol copolymer, and an inner water-blocking wall formed from a polyamide such as Nylon 11 or Nylon 12. In DE 40 06 870, a fuel line is proposed in which an intermediate solvent barrier layer is formed of unmodified Nylon 6.6 either separately or in combination with blends of polyamide elastomers. The internal layer is also composed of polyamides, preferably modified or unmodified Nylon 6. The outer layer is composed of either Nylon 6 or Nylon 12.

Another tubing designed to be resistant to alcoholic media is disclosed in UK Application Number 2 204 376 A in which a tube is produced which has an thick outer layer composed of 11 or 12 block polyamides such as

Nylon 11 or Nylon 12 which may be used alone or combined with 6 carbon block polyamides such as Nylon 6 or 6.6 Nylon. The outer layer may be co-extruded with an inner layer made from alcohol-resistant polyolefin co-polymer such as a co-polymer of propylene and maleic acid. The inner layer is zinc chloride resistant Nylon 6.

Heretofore it has been extremely difficult to obtain satisfactory lamination characteristics between dissimilar polymer layers. Thus all of the multi-layer tubing proposed previously has employed polyamide-based materials in most or all of the multiple layers. While many more effective solvent-resistant chemicals exist, their use in this area is limited due to limited elongation properties, strength and compatibility with Nylon 11 and 12.

Thus it would be desirable to provide a tubing material which could be employed in motor vehicles which would be durable and prevent or reduce permeation of organic materials therethrough. It would also be desirable to provide a tubing material which would be essentially nonreactive with components of the liquid being conveyed therein.

## SUMMARY OF THE INVENTION

The present invention is a multi-layer tube which can be used on motor vehicles for applications such as in a fuel line or a vapor return or recovery line. The tube of the present invention is composed of:

a thick flexible outer tubing having an inner and an outer face, the outer tubing consisting essentially of an extrudable melt processible 6 carbon block polyamide thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C;

a thin intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable melt processible

thermoplastic capable of sufficiently permanent laminar adhesion to the outer tubing; and

an inner hydrocarbon barrier layer bonded to the intermediate bonding layer, the inner layer consisting of an extrudable melt processible 6-carbon block polyamide thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer.

DESCRIPTION OF THE DRAWING

The objects, features and advantages of the present invention will become more readily apparent from the following description, reference being made to the following drawing in which the Figure is a sectional view through a piece of tubing of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is a multi-layer fuel line and vapor tube which contains at least one bonding layer and at least an outer and an inner tubing layer. The tubing of the present invention is, preferably, fabricated by co-extruding given thermoplastic materials in a conventional co-extrusion process. The tubing may either be co-extruded to a suitable length or may be co-extruded in continuous length and cut to fit the given application subsequently. The tubing of the present invention may have an outer diameter up to 50 mm. However, in applications such as fuel lines and vapor recovery systems, outer diameter of up to 2 inches are preferred.

The material may have any suitable wall thickness desired. However, in automotive systems such as those described herein, wall thicknesses between 0.5 mm and 2 mm are generally employed with wall thicknesses of approximately 0.8 to 1.5 mm being preferred. While it is within the scope of this invention to prepare a tubing material having a plurality of overlaying layers of various thermoplastic materials, the tubing of the present invention generally has a maximum of five layers

inclusive of the bonding layers. In the preferred embodiment, the tubing material has three or four.

The tubing 10 of the present invention is a material which is suitable for use in motor vehicles and comprises a relatively thick outer layer 12 which is non-reactive with the external environment and can withstand various shocks, vibrational fatigue, and changes in temperature as well as exposure to various corrosive or degradative compounds to which it would be exposed through the normal course of operation of the motor vehicle.

It is anticipated that both the outer tubing layer 12 as well as any interior layers bonded thereto would be suitable for use at an outer service temperature range between about -40°C and about 150°C, with a range of -20°C to 120°C being preferred. The various layers of tubing are integrally laminated to one another and resistant to delamination throughout the lifetime of the tubing. The tubing thus formed will have a tensile strength of no less than 25N per mm square and an elongation value of at least 150%. The tubing will have a burst strength at 23°C and 120°C of at least 20 bar. The multi-layer tubing of the present invention is sufficiently resistant to exposure to brake fluid, engine oil and peroxides such as those which may be found in gasoline.

The outer layer 12 may be composed of any melt-processible extrudable thermoplastic material which is resistant to ultra violet degradation, extreme changes in heat and exposure to environmental hazards such as zinc chloride, and degradation upon contact with engine oil and brake fluid. In general, the exterior layer consists essentially of 6-carbon block polyamides, such as Nylon 6, which are resistant to degradation upon exposure to zinc chloride.

The materials which compose the outer layers can be employed in their respective unmodified states or

can be modified with various plasticizers, flame retardants and the like in manners which would be known to one reasonably skilled in the art.

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The Nylon 6 which composes the outer layer can be employed can also be modified with various plasticizers, flame retardants and the like in manners which would be known to one reasonably skilled in the art.

In the preferred embodiment, the outer layer is composed of a polyamide thermoplastic derived from the condensation polymerization of caprolactam. Such materials are commonly referred to as 6-carbon block polyamides or Nylon 6. In the preferred embodiment, the 6-carbon block polyamide contains sufficient quantities of modifying agents to impart a level of zinc chloride resistance greater than or equal to that required by test method SAE J844; non-reactivity after 200 hour immersion in a 50% by weight aqueous zinc chloride solution. In the preferred embodiment, the 6-carbon block polyamide material is a multi-component system comprised of a Nylon-6 copolymer blended with other Nylons and olefinic compound. The zinc-chloride resistant Nylon-6 of choice will have a melt temperature between about 220°C and 240°C. Examples of thermoplastic materials suitable for use in the tubing of the present invention are propriety materials which can be obtained commercially under the

tradenames M-7551 from NYCOA Corporation and ALLIED 1779 from Allied Chemical.

The 6-carbon black polyamide may, optionally, include other modifying agents such as various plasticizing agents generally present in amounts between about 1.0% and about 13% by total weight of the thermoplastic composition. as are readily known in the art. The polyamide material employed, preferably, is an impact-modified material capable of withstanding impacts of at least 2 ft. lbs. at temperatures below about -20°C.

The outer layer 12 has a wall thickness sufficient to provide suitable strength an endurance to the multi-layer tubing of the present invention. In applications involving automotive vehicles, the outer layer 12 comprises between about 50% and about 60% of the total wall thickness. In general, the outer layer has a wall thickness between about 0.5 mm and about 0.8 mm; with a preferred wall thickness between about 0.6 mm and about 0.7 mm. As indicated previously, the material can be extruded by conventional co-extrusion methods to any continuous length desired.

The intermediate bonding layer 14 is integrally bonded to the inner surface of the thick outer polyamide layer 12. In the present invention, the intermediate bonding layer 14 is a chemically dissimilar permeation resistant, chemical resistant, fuel resistant thermoplastic material which is melt processible in normal ranges of extrusion, i.e. about 175° to about 250°C. By the term "chemically dissimilar" it is meant that the intermediate bonding layer 14 consists essentially of a non-polyamide material which is capable of adhesion to a bonding layer interposed between the thick outer layer and the inner layer in a manner which will be described subsequently.

In the preferred embodiment, the thermoplastic material which comprises the intermediate bonding layer is a thermoplastic material selected from the group

consisting of co-polymers of substituted or unsubstituted alkenes having less than four carbon atoms and vinyl alcohol, alkenes having less than four carbon atoms and vinyl acetate, and mixtures thereof. In the preferred embodiment, the thermoplastic material employed will be resistant to permeation by and interaction with short chain aromatic and aliphatic compounds such as those which would be found in gasoline.

The preferred material is a copolymer of ethylene and vinyl alcohol which has an ethylene content between about 27% and about 35% by weight with an ethylene content between about 27% and about 32% being preferred. Examples of suitable materials which can be employed in the tubing of the present invention include: ethylene vinyl alcohol commercially available from EVA/LA.

The thermoplastic material employed in the intermediate bonding layer 14 is capable of serving as a hydrocarbon barrier to prevent significant permeation of the aromatic and aliphatic components of gasoline through to the polyamide outer layer of the tubing and thus, out to the surrounding environment. The effectiveness of the barrier layer at preventing such permeation will vary depending on numerous factors including but not limited to the thickness and composition of the inner layer, the thickness of the bonding layer and the composition of the materials conveyed through the tubing. In the preferred embodiment, it is anticipated that the bonding layer will be capable of providing the tubing of the present invention with a passive hydrocarbon permeation level less than about 0.5 $g/m^2$ per 24 hour.

The material employed in the intermediate bonding layer 14 can, optionally, exhibit conductive characteristics rendering it is capable of dissipation of electrostatic charges in the range of $10^{-4}$ to $10^{-9}$ $ohm/cm^2$. The thermoplastic material employed in the present invention may include, in its composition, a

conductive media in sufficient quantity to permit electrostatic dissipation in the range defined. The conductive media may be any suitable material of a composition and shape capable of effecting this static dissipation. The conductive material may be selected from the group consisting of elemental carbon, stainless steel and highly conductive metals such as copper, silver, gold, nickel, silicon and mixtures thereof. The term "elemental carbon" as used herein is employed to describe and include materials commonly referred to as "carbon black". The carbon black can be present in the form of carbon fibers, powders, spheres, and the like.

The amount of conductive material contained in the thermoplastic is generally limited by considerations of low temperature durability and resistance to the degradative effects of the gasoline or fuel passing through the tubing. The amount of conductive material employed may be that amount sufficient to impart electrostatic dissipation characteristics to the tubing. When employed, the maximum amount of conductive material in the thermoplastic material is less than 5% by volume.

The conductive material can either be interstitially integrated into the crystalline structure of the polymer or can be co-polymerized therewith. Without being bound to any theory, it is believed that carbon-containing materials such as carbon black may be subject to carbon co-polymerization with the surrounding thermoplastic material. Materials such as stainless steel are more likely to be interstitially integrated into the crystalline structure of the polymer.

The intermediate bonding layer 14 serves to bond the thick outer layer 12 to the inner layer 16 to form a secure laminar bond therebetween. The inner layer 16 provides a stable fuel-contacting surface on the interior of the tube 10.

The inner layer 16 may be composed of any melt-processible extrudable thermoplastic material which is

resistant to ultra violet degradation, extreme changes in heat and exposure to gasoline and its additives. The material of choice may also exhibit resistance to environmental hazards such as exposure to zinc chloride, and resistance to degradation upon contact with materials such as engine oil and brake fluid.

The preferred material is a polyamide derived from the condensation polymerization of caprolactam. Suitable materials are commonly referred to as 6-carbon block polyamides or Nylon 6. The 6-carbon block polyamides employed herein may contain various plasticizers, fire retardants and the like as well as sufficient quantities of modifying agents to impart a level of zinc chloride resistance greater than or equal to that required by test method SAE J844: i.e. non-reactivity after 200 hour immersion in a 50% by weight aqueous zinc chloride solution.

In the preferred embodiment, the 6-carbon block polyamide material employed is a multi-component system comprised of a Nylon-6 copolymer blended with other Nylons and olefinic compounds. The 6-carbon block polyamide material of choice will is preferably resistant to zinc chloride and has a melt temperature between about 220°C and 240°C. Examples of thermoplastic materials suitable for use in the tubing of the present invention are propriety materials which can be obtained commercially under the tradenames M-7551 from NYCOA Corporation and ALLIED 1779 from Allied Chemical.

In instances where the 6-carbon block polyamide material includes plasticizing agents, these materials are generally present in amounts between about 1.0% and about 13% by total weight of the thermoplastic composition. The polyamide material employed, preferably, is an impact-modified material capable of withstanding impacts of at least 2 ft. lbs. at temperatures below about -20°C.

The inner layer 16 may also contain suitable material in sufficient quantities to impart electrostatic conductivity characteristics to the tubing of the present invention. When employed, the material is preferably capable of dissipation of electrostatic charges in the range of $10^{-4}$ to $10^{-9}$ ohm/cm$^2$. The thermoplastic material employed in the present invention may include, in its composition, a conductive media in sufficient quantity to permit electrostatic dissipation in the range defined. The conductive media may be any suitable material of a composition and shape capable of effecting this static dissipation. The conductive material may be selected from the group consisting of elemental carbon, stainless steel and highly conductive metals such as copper, silver, gold, nickel, silicon and mixtures thereof. The term "elemental carbon" as used herein is employed to describe and include materials commonly referred to as "carbon black". The carbon black can be present in the form of carbon fibers, powders, spheres, and the like.

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steel are more likely to be interstitially integrated into the crystalline structure of the polymer.

In the preferred embodiment, the inner layer has the minimum wall thickness sufficient to achieve the permeation resistance desired. In general, the inner layer is thinner than the outer layer with the thickness of the outer layer being between about 50% and about 60% of the total wall thickness of the tubing or between 55% and 60% of the thickness of the thick outer layer. In the specified embodiment, the inner wall thickness is between about 0.01 mm and about 0.2 mm with a thickness of about 0.05 mm to about 0.17 mm being preferred. The intermediate bonding layer generally may have a thickness less than or equal to that of the inner layer.

The intermediate bonding layer is of sufficient thickness to permit an essentially homogeneous bond between the inner and outer layers. In general, the intermediate bonding layer can be thinner than the other two layers and can constitute between about 10% and about 50% of the total wall thickness or between about 20% and about 30% of the thickness of the outer layer. In the specified embodiment, the thickness of the intermediate bonding layer is between about 0.01 mm and about 0.25 mm with a thickness between about 0.05 mm and about 0.20 mm being preferred.

The total wall thickness of the tubing of the present invention is generally between about 0.5 mm and about 2.0 mm with a wall thickness between about 0.8 and about 1.25 mm being preferred.

The tubing of the present invention may also, optionally include an outer jacket (not shown) which surrounds the outer layer. The fourth outer jacket may be either co-extruded with the other layers during the extrusion process or may be put on in a subsequent process such as cross-extrusion. The outer jacket may be made of any material chosen for its structural or insulative characteristics and may be of any suitable

wall thickness. In the preferred embodiment, the outer jacket may be made of a thermoplastic material selected from the group consisting of zinc-chloride resistant Nylon 6, Nylon 11, Nylon 12, polypropylene, and thermoplastic elastomers such as SANTOPRENE, KRATON, VICHEM and SARLINK. If desired, these materials may be modified to include flame retardants, plasticizers and the like.